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XVII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

TRINITROPHENYLMALONIC ESTER.

By C. Loring Jackson and C. A. Soch.

Presented May 9, 1894.

At the end of his paper on the action of sodium acetacetic ester on picrylchloride, Dittrich* states that, in spite of many and varied attempts, he had not succeeded in making a picrylmalonic ester from picrylchloride and sodium malonic ester, but that he obtained in every case sodic picrate and viscous products of the decomposition of the malonic ester. This statement impressed us as a strange one, since in work † done in this Laboratory it had been found that tribromdinitrobenzol acted much more easily with sodium malonic ester than with sodium acetacetic ester; for whereas a good yield of the substituted malonic ester could be obtained even when the reaction took place in the cold, with the acetacetic ester the yield was small even after the reagents had been boiled together. Accordingly, we took up the study of this subject, and found, as we had expected, that the picrylmalonic ester could be obtained without difficulty. It is a white substance melting at 59°, and forms a blood-red sodium salt, which is tolerably stable, dissolving in water without decomposition. The picrylbrommalonic ester $C_6H_2(NO_2)_3CBr(COOC_2H_5)_2$ was made by treating the substituted malonic ester with an excess of bromine; it melts at 85°–86°. One object in undertaking this work was to see whether any trinitrobenzol was formed in the action of sodium malonic ester or sodium acetacetic ester on picrylchloride by the replacement of the atom of chlorine by hydrogen after the analogy of such reductions, which have been noticed frequently in the work done in this Laboratory upon tribromdinitrobenzol and tribromtrinitrobenzol. Unfortunately the research was begun so late in the year that we have been unable to arrive at a definite conclusion on this subject, and it is hoped that it will be possible to repeat the experiments on a larger scale and with conclusive results early in the coming term. A bromdinitrophenylbrommalonic ester corresponding to the picryl compound mentioned above was also prepared. It melts at 72°–73°.

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* Ber. d. ch. G., XXIII. 2720.

† These Proceedings, XXIV. 2, 274.

Trinitrophenylmalonic Ester (*Picrylmalonic Ester*), $C_6H_2(NO_2)_3CH(COOC_2H_5)_2$.

As Dittrich* states that the product of the reaction of picrylchloride and sodium malonic ester is viscous, we first turned our attention to the preparation of the sodium salt of the substituted malonic ester in the hope that this might be purified more easily than the free ester.

Sodium Picrylmalonic Ester, $C_6H_2(NO_2)_3CNa(COOC_2H_5)_2$.

The picrylchloride used in making this substance was prepared according to the method of Clemm,† except that we crystallized the chloride from a mixture of chloroform and alcohol, as we found that the addition of the chloroform made it possible to work with much smaller volumes of the solvent, and also seemed to prevent in great measure the deposition of the picrylchloride in an oily form. A strong cold benzol solution of 10 grams of this picrylchloride was mixed with an alcoholic solution of sodium malonic ester made from 14 grams of malonic ester and the sodic ethylate from 2.1 grams of metallic sodium. The mixture, which took on at once a deep red color, was cooled at first, and then allowed to stand for twelve hours at ordinary temperatures; after which it was diluted with about three quarters of a litre of water. In this way a red aqueous solution was obtained, and a supernatant layer of benzol which contained a portion of the picrylmalonic ester formed, while the rest was dissolved as a sodium salt in the red aqueous solution, in addition to some sodic picrate and the sodic chloride. Upon acidifying the aqueous liquid with sulphuric acid a yellow precipitate was thrown down, which as it settled from the liquid collected in an oily state on the bottom of the beaker. To the oily product a strong solution of sodic hydrate was added, which imparted to it a dark red color, and after thorough mixing converted it into a red crystalline solid. To remove any liquid or viscous impurities from the salt, it was next dissolved in the smallest possible amount of alcohol and treated with an excess of benzol, after which the mixed solutions were evaporated cautiously on the steam bath until crystals began to form, when upon cooling the sodium salt was obtained in fine red crystals; these were washed with benzol, and after drying in a desiccator gave the following results on analysis: —

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* Ber. d. ch. G., XXIII. 2720.

† Journ. Prakt. Chem., [2.], I. 145.

I. 0.2400 gram of the substance after evaporation with sulphuric acid gave 0.0427 gram of sodic sulphate.

II. 0.8331 gram of the substance gave 0.1429 gram of sodic sulphate.

	Calculated for $C_6H_2(NO_2)_3CNa(COOC_2H_5)_2$.	Found I.	Found II.
Sodium	5.85	5.76	5.56

An additional quantity of the salt was obtained by the treatment just described from the residue left after evaporating off the benzol from the solution of picrylmalonic ester in this solvent obtained by adding water to the product of the reaction.

Properties of the Sodium Salt of Picrylmalonic Ester. — It crystallizes from a mixture of alcohol and benzol in dark red crystals often a centimeter long. It is easily soluble in alcohol or ether; somewhat less soluble in water than in alcohol; nearly insoluble in benzol. It does not seem to be decomposed by any of these solvents. Strong sulphuric acid decomposes it, but without any explosion, which surprised us, as it showed a tendency to explode when dry even at comparatively low temperatures.

As the potassium salt of picric acid is so much less soluble than the sodium salt, we prepared the potassium salt of the picrylmalonic ester by treating the free ester with potassic hydrate in strong aqueous solution; but, although this salt was somewhat less soluble in both water and alcohol than the sodium salt, the difference was not very marked, and there would be no advantage in using the potassium salt instead of the sodium salt in the purification of the substance.

The behavior of an aqueous solution of the sodium salt of picrylmalonic ester with various reagents was also studied, and the following more or less characteristic precipitates were obtained: —

Salt of magnesium, heavy reddish flocks.

Salts of calcium or barium, granular or crystalline precipitates of an amethyst color.

Salt of manganese, dirty yellow flocks.

Salt of nickel, light red flocks.

Salts of lead or silver, dark red flocks.

Salt of cadmium, reddish yellow flocks.

Picrylmalonic Ester, $C_6H_2(NO_2)_3CH(COOC_2H_5)_2$.

Although in our earlier experiments we prepared this substance through its sodium salt on account of the discouraging statements of Dittrich, we soon found that this was unnecessary, as the substance could be purified directly without difficulty, and in all our later work we have adopted this direct method, which we are about to describe, as it is much more convenient than the method of purification by means of the sodium salt. To prepare the picrylmalonic ester we proceeded according to the method described under Sodium Picrylmalonic Ester, until by the addition of water the product had been divided into an aqueous and a benzol solution. The aqueous solution after acidification with dilute sulphuric acid was allowed to stand until the oily precipitate had separated completely from the mass of the liquid; part of it settled, part floated on the surface, and even during this comparatively short standing the floating part was converted into crystals, which could be used to promote the crystallization of the larger quantity on the bottom of the beaker. This solidification of the main portion of the oily product was effected without difficulty by cooling with running water, one of the crystals from the surface of the water being added if necessary; and the solidified product, after washing with cold water, was crystallized from alcohol. The benzol solution, which had been separated from the aqueous solution, was acidified with dilute sulphuric acid, and allowed to evaporate spontaneously, when it furnished a rather large additional quantity of the oily product, which however, did not solidify so easily as that obtained from the aqueous portion, since it was necessary to allow it to stand for three or four days with occasional stirring in order to bring it into a crystalline condition. It was then pressed between layers of filter paper, which removed an oily impurity, after which it was mixed with the crystals obtained from the aqueous liquid, and the whole purified by crystallization from alcohol until it showed the constant melting point 59°, when it was dried in a desiccator, and analyzed with the following results: —

I. 0.2707 gram of the substance gave 28.6 c.c. of nitrogen at a temperature of 25° and a pressure of 757.4 mm.

II. 0.2565 gram gave 25.9 c.c. of nitrogen at a temperature of 22° and a pressure of 755.8 mm.

	Calculated for $C_6H_2(NO_2)_3CH(COOC_2H_5)_2$.	Found.	
		I.	II.
Nitrogen	11.32	11.75	11.38

It is worthy of remark that, whereas Dittrich from the action of picrylchloride on sodium acetacetic ester obtained a considerable quantity of dipicrylacetacetic ester, our principal product was the monopicrylmalonic ester, and only on one occasion have we observed a trace of a substance with a much higher melting point, which we took to be the dipicryl compound. We should add that, in applying the same method to the action of sodium acetacetic ester on picrylchloride, we obtained almost exclusively monopicrylacetacetic ester.

Properties of Picrylmalonic Ester. — It crystallizes from alcohol in white, long, rather slender rectangular plates, which develop into rather thick prisms with blunt ends often as much as two centimeters long. It melts at 59°, and is very soluble in chloroform, ether, benzol, or glacial acetic acid; somewhat less soluble in carbonic disulphide; soluble in cold alcohol, freely in hot; rather more soluble in methyl than in ethyl alcohol; insoluble in ligroine or cold water, slightly soluble in hot water. All the solutions of this substance except that in glacial acetic acid have a pink color, which is the more marked the stronger the solution, and the alcoholic solution imparts to the fingers a crimson color not unlike rosaniline, although less purple. This coloration of the fingers is much deeper than the color of the solution, and is tolerably fast. The formation of these pink or crimson colors from the white crystals is striking, and will be more carefully studied.

Cold strong sulphuric acid dissolves it; if this solution is warmed it turns red, and gives off bubbles of gas; dilution of the red solution after it had cooled precipitated a yellow solid. Strong nitric acid acted in the same way, except that the picrylmalonic ester dissolves more slowly in cold nitric acid than in sulphuric acid. Strong hydrochloric acid did not dissolve it in the cold, but on warming the substance melted, and then went into solution very slowly. The picrylmalonic ester has well marked acid properties forming the red sodium salt when treated with an aqueous solution of sodic hydrate. As is often the case with substances of this class, the sodium salt is nearly insoluble in a strong solution of sodic hydrate. The sodium salt is also formed by the action of a solution of sodic carbonate on the free ester.

Trinitrophenylbrommalonic Ester (Picrylbrommalonic Ester), $C_6H_2(NO_2)_3CBr(COOC_2H_5)_2$.

This substance was made by dissolving some of the trinitrophenylmalonic ester described in the preceding section in a small quantity of glacial acetic acid, and adding liquid bromine until it was present in distinct excess, as shown by the reddish brown color of the liquid. To make certain that the reaction was complete, the liquid was warmed gently on the steam bath for a few minutes, and then allowed to stand at ordinary temperatures for an hour, after which water was added in excess, giving a pale yellow precipitate partly solid and partly liquid. After this had settled, the supernatant liquid, colored red with the excess of bromine, was poured off, and the liquid part solidified by cooling. It was then washed with water, dried by pressure on filter paper, and purified by recrystallization from alcohol until it showed the constant melting point 85°–86°, when it was dried in a desiccator, and analyzed with the following result: —

0.1873 gram of the substance gave by the method of Carius 0.0789 gram of argentic bromide.

	Calculated for $C_6H_2(NO_2)_3CBr(COOC_2H_5)_2$.	Found.
Bromine	17.78	17.93

It is obvious that this atom of bromine, the presence of which is shown by the analysis, may have entered the molecule in one of two different places, either replacing the hydrogen of the malonic ester radical, as in the formula given above, or replacing one of the atoms of hydrogen attached to the benzol ring. It is easy to determine which position the bromine occupies, for, if it is attached to the malonic ester radical, the substance will have lost all its acid properties, since the acid hydrogen has been replaced by the atom of bromine. In the second case, where the bromine is attached to the benzol ring, on the other hand, the acid properties will not be interfered with, but on the contrary will be somewhat increased if the bromine atom has any effect whatever. Upon treating our new substance with a solution of sodic carbonate no change was observed, whereas the picrylmalonic ester is converted at once into its red salt by this reagent; as, therefore, this substance has no acid properties, it follows that the bromine has entered the malonic ester radical, and the formula given above is the correct one.

Properties of Picrylbrommalonic Ester. — It crystallizes from alcohol in white plates, nearly but not quite square, and much striated; these plates are arranged in irregular rather long rosettes. Less commonly it occurs in bladed or pennate forms. In general appearance it resembles acetanilid. It melts at 85°–86°, and is very soluble in chloroform or benzol; rather less soluble in ether, carbonic disulphide, or glacial acetic acid; soluble in cold alcohol, freely soluble in hot; rather more soluble in methyl than in ethyl alcohol; insoluble in cold ligroine, soluble in it when hot although with some difficulty; essentially insoluble in water, whether hot or cold. The best solvent for it is alcohol. Its alcoholic solution shows a faint pink color, similar to that given by picrylmalonic ester, but less marked. Strong sulphuric acid dissolves it in the cold with a yellow color; upon warming this solution it becomes brownish black, and bubbles of gas are given off. Strong hydrochloric acid seems to have no action on it even when hot. In cold strong nitric acid it is insoluble, but dissolves easily if the acid is hot, and boiling this solution for a short time produces no signs of decomposition. A strong solution of sodic hydrate did not act upon it in the cold, but, when heated with it, gave a red solution. The solution here was undoubtedly preceded by removal of the bromine. As has been stated already, sodic carbonate does not act on this substance.

Bromdinitrophenylbrommalonic Ester, $C_6H_2Br(NO_2)_2CBr(COOC_2H_5)_2$.

This substance was made by dissolving the bromdinitrophenylmalonic ester in glacial acetic acid and adding to the strong solution an excess of liquid bromine. The bromdinitrophenylmalonic ester was made from tribromdinitrobenzol melting at 192° and sodium malonic ester.* After an excess of bromine had been added, as shown by the color, the liquid was warmed gently on the water bath for a short time, and, if the color had disappeared, more bromine added. It was then, after it was cool, precipitated with water, and the substance obtained solidified by cooling, if necessary; after which it was purified by crystallization from alcohol, until it showed the constant melting point 72°–73°. It is not wise, however, to rely on the melting point as the only proof of purity, since the bromdinitrophenylmalonic ester from which it is formed melts at 75°–76°; we have therefore always tested our product also with a solution of sodic hydrate, which gives a red salt with the mother substance, but has no effect in the cold on the desired compound. After purification it was dried in a desiccator, and analyzed with the following results: —

I. 0.3196 gram of the substance gave by the method of Carius 0.2451 gram of argentic bromide.

II. 0.1997 gram of the substance gave 0.1550 gram of argentic bromide.

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* These Proceedings, XXIV. 2.

	Calculated for $C_6H_2Br(NO_2)_2CBr(COOC_2H_5)_2$	Found. I.	Found. II.
Bromine	33.05	32.64	33.02

The fact that this substance is not acted on by cold sodic hydrate proves that it contains the second atom of bromine attached to the malonic ester radical and not to the benzol ring.

Properties of Bromdinitrophenylbrommalonic Ester. — It crystallizes from alcohol in long white prisms terminated by a single plane at an acute angle and arranged in radiated groups; these crystals are sometimes a centimeter long. It melts at 72°–73°, and is very soluble in benzol, chloroform, acetone, carbonic disulphide, or glacial acetic acid; not freely soluble in cold alcohol, but easily in hot; more soluble in methyl than in ethyl alcohol; insoluble in cold ligroine, slightly soluble in hot; insoluble in water, but if boiled with water for some time, fresh water being added to take the place of that which evaporates, it is finally brought completely into solution. This action is undoubtedly due to the removal of the side-chain bromine as hydrobromic acid. It will be studied more carefully hereafter. Strong sulphuric acid does not act upon it in the cold, and when hot it acts only very slowly. Strong nitric acid also has no action when cold, but if hot dissolves it. Strong hydrochloric acid does not act upon it in the cold, and when hot has rather less effect than sulphuric acid. Strong solutions of sodic hydrate and ammonic hydrate have little or no action in the cold; when warmed they convert it into a red substance, probably a salt formed after the removal of the side-chain atom of bromine. The whole subject of the replacement of this second atom of bromine by other radicals must be studied more carefully before any account can be given of it. It is hoped that this work can be carried on in this Laboratory during the coming term.